Ultrasonic investigation of the states of water in hydrogels

Shinobu Koda*, Kiyoo Yamashita, Satoshi Iwai and Hiroyasu Nomura
Department of Chemical Engineering, School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan

and Masashi Iwata
Department of Industrial Chemistry, Suzuka National College of Technology, Shiroko-cho, Suzuka, Mie 510-02, Japan
(Received 9 March 1994; revised 25 July 1994)

The longitudinal sound velocities in crosslinked polyacrylate hydrogels were measured as a function of water content in the gel in the temperature range 30–100°C. The sound velocity changed drastically around a water content of 40–50 wt%. Above this range, the sound velocity decreased monotonically and approached that of pure water. The maximum sound velocity was observed around 74°C for a water content above 50 wt%, while for a water content less than ca. 40 wt% the temperature dependence curve of the sound velocity became concave. The amount of water bound to the gel was estimated and was discovered to vary depending on the ratio of sodium polyacrylate to polyacrylic acid and the temperature.

(Keywords: hydrogel; sodium polyacrylate gel; bound water)

INTRODUCTION

Hydrogels can absorb large amounts of water and drastically increase in volume. Some hydrogels swell to several hundred times their original volume. The hydration power or water absorptivity of the hydrogel is one important factor which determines the functionality and the quality of the hydrogel. It is well known that the physicochemical properties of the hydrogel depend not only on the molecular structure, the gel structure and the degree of crosslinking but also on the states of water in the hydrogel. In addition, the study of the states of water in the gel is important to elucidate the role of water in biomasses.

Various experimental methods have been used to study the states of water in the gel. The main experimental methods are differential scanning calorimetry (d.s.c.)[1–7] and n.m.r.[8–15]. The d.s.c. data are obtained by cooling or heating the hydrogel, and this leads to an estimate of the amount of non-freezable water or bound water. Therefore, it is difficult to elucidate the states of water in a gel in a thermal equilibrium state. Katayama and Fujiwara suggested that four thermal equilibrium states exist depending on the temperature and that hysteresis effects should be taken into account in the d.s.c. data[8,9]. The n.m.r. method produces relaxation times T_1 and T_2 which reflect the dynamic nature of water molecules. From d.s.c. and n.m.r. studies, the states of water in synthesized hydrogels are classified into three states: free water, non-freezable bound water and an intermediate state. Though it is difficult to characterize clearly the intermediate state, the amount of bound water in most polymers, gels and biopolymers is between 0.3 and 0.5 g per gram of dry polymer.

The mechanical properties of the hydrogel, such as elasticity, compressibility and rigidity, are also affected by the states of water in the gel[6]. Adiabatic compressibility is evaluated from sound velocity and density data. As the compressibility is sensitive to changes in the states of water in the hydrogel, the sound velocity gives information on hydration, or the water absorbed in the hydrogel. Recently, Vanderwal *et al.* have studied the states of water in the hydrogel of poly(2-hydroxyethyl methacrylate) by the Brillouin scattering method[16]. They estimated the amount of bound water from the Brillouin shift obtained in the gigahertz region. The Brillouin scattering method is unsuitable for measuring the sound velocity in an opaque sample. However, the pulse method is suitable for measuring the sound velocities in many polymers even if they are not transparent.

Crosslinked polyacrylate hydrogel contains sodium polyacrylate and polyacrylic acid. Though the hydrogel is used in industrial and agricultural applications, little work on the states of water in crosslinked polyacrylate hydrogel has been carried out from the viewpoint of compressibility. The purpose of the work described in this paper is to investigate the states of water in crosslinked polyacrylate hydrogel from measurements of sound velocity and compressibility.

EXPERIMENTAL

Samples

Crosslinked polyacrylate gels with different ratios of sodium polyacrylate (NAPA) and polyacrylic acid (PAA)

---

* To whom correspondence should be addressed

0032-3861/94/26/5626–04

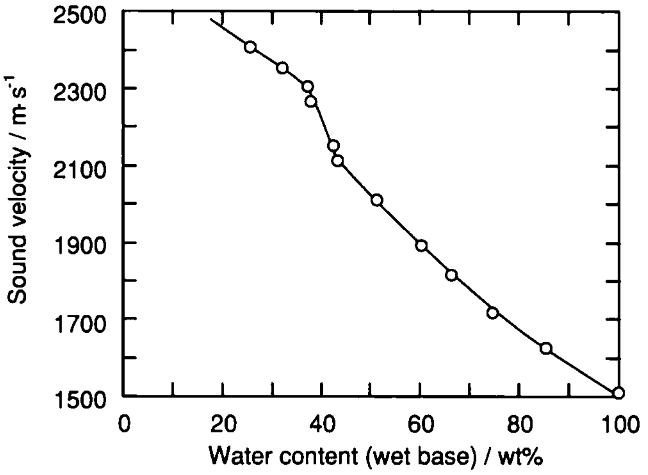

Figure 1 Plot of sound velocity in the hydrogel *versus* water content at 30°C for 3/1 NAPA/PAA

were kindly supplied by Toa Gohsei Chemicals. Measurements were made on hydrogels with a NAPA/PAA composition ratio from 0/1 to 19/1. Starting with synthesized hydrogels with a water content of about 57 wt%, samples with different water contents were prepared by drying or swelling. To determine the water content, the sample gel was weighed, completely dehydrated and then weighed again.

Measurements

The sound velocity was obtained from measurement of the time required for transmission through a hydrogel of thickness l. A hydrogel with a cross-section of $4\,cm^2$ and a thickness of 5–6 mm was prepared for the measurement. The transmission time t was measured using the time to amplitude converter (TAC) method[17–20]. A cross-cut quartz crystal operating at 5 MHz was used as a transducer. The sound velocity was calculated from

$$V = l/t \qquad (1)$$

The temperature was regulated with an air thermostat to within 0.1°C and was increased from 30 to 110°C at a heating rate of $0.3°C\,min^{-1}$. The water content in the hydrogel decreased by ca. 2 wt% after heating the hydrogel from 30 to 100°C. Details of the apparatus and experimental method are given in a previous paper[20]. The experimental error in sound velocity was within $3\,m\,s^{-1}$.

The density of the hydrogel ρ was measured with a Beckman densitometer manufactured by Toshiba-Beckman.

The adiabatic compressibility β was calculated from

$$\beta = 1/\rho V^2 \qquad (2)$$

RESULTS

Figure 1 shows the sound velocity as a function of water content in a hydrogel with a 3/1 NAPA/PAA ratio. The sound velocity increases with decreasing water content, and a sharp increase in the sound velocity is observed near a water content of 50 wt%. Thereafter, the sound velocity smoothly increases with decreasing water content again. Extrapolation of the water content in the hydrogel to zero gives the sound velocity of the crosslinked polymer itself – ca. $2600\,m\,s^{-1}$. This value is larger in comparison with the velocities in other ordinary polymers[21], which are around $2000\,m\,s^{-1}$. This indicates that crosslinked polyacrylate polymers are more rigid than other linear polymers. The sudden change in the sound velocity reflects an alteration in the states of water in the hydrogel. The states of water in the hydrogel are roughly classified into two groups. One is free water and the other is bound water. When the water content is low, it is assumed that all water molecules in the gel are bound. Above a certain water content, some of the water molecules are bound and the remainder are free[1–7]. The sharp increase in the sound velocity around a water content of 50 wt% is caused by the loss of free water. With a further decrease in water content, only the bound water is left in the gel. The amount of bound water estimated from *Figure 1* is 40 wt%, i.e. 0.7 g of water per gram of dry polymer. It is well known that the amount of bound water in homopolymers ranges from 0.3 to 0.4 g per gram of dry polymer. The amount of bound water in hydrogels is slightly larger than that in homopolymers. However, the slightly larger amount of bound water should not be responsible for the high ability for water absorption of hydrogels.

In *Figure 2*, the density of the hydrogel is plotted against water content. The density of the dry gel is $1.9\,g\,cm^{-3}$. The density of the gel decreases as the water content increases, within experimental error. The adiabatic compressibilities can be calculated from equation (2) and the results are shown in *Figure 3*. A breaking point in the adiabatic compressibility is also observed, as expected from *Figure 1*. The hydrogel with a lower water content has a higher rigidity, and as the water content increases, the compressibility of the hydrogel approaches that of pure water.

Figure 4 shows the relationships between the temperature and the sound velocity in the hydrogel for different water contents. With large amounts of water, the relationship shows a concave curve. It is well known that the sound velocity in pure water reaches its maximum at 74°C[22]. This is characteristic of pure water and is explained in terms of the change in the water structure. The presence of a maximum in sound velocity

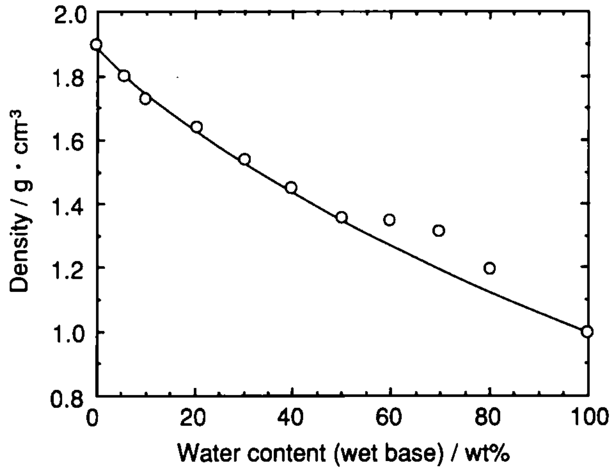

Figure 2 Plot of density of the hydrogel *versus* water content at 30°C for 3/1 NAPA/PAA

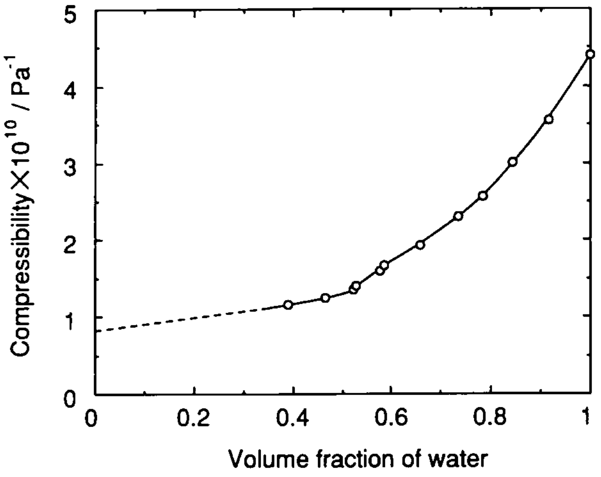

Figure 3 Plot of adiabatic compressibility of the hydrogel *versus* water content for 3/1 NAPA/PAA

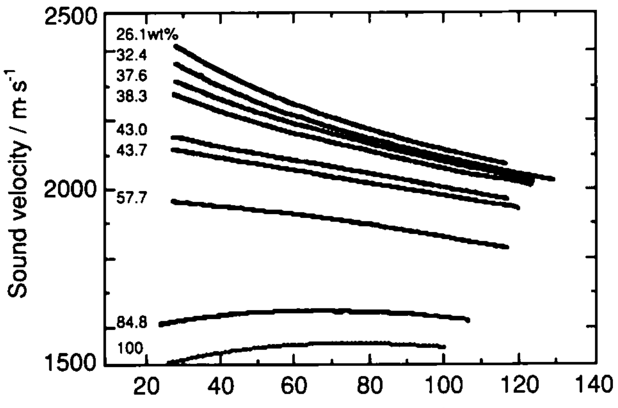

Figure 4 Plots of sound velocity in the hydrogel *versus* temperature for various water contents in 3/1 NAPA/PAA

against temperature means that some of the water in the hydrogel begins to behave like bulk water, i.e. free water. This fact is consistent with the observation of a sudden sound velocity change in *Figure 1* and a breaking point in the adiabatic compressibility in *Figure 3*.

In *Figure 5*, the variations in sound velocity for different compositions of PAA and NAPA are shown. The sound velocities for samples with 0/1, 9/1 and 19/1 NAPA/PAA ratios increase with decreasing water content and no abrupt change in sound velocity is observed at any level of water content investigated. In general, bound water has been recognized in most gel investigations so far[23-30]. In the case of the sample with no NAPA content (0/1), the change in the sound velocity against water content is small and it is difficult to specify a breaking point, which may be observed below ca. 30 wt%. On the other hand, for the samples with high NAPA contents (9/1 and 19/1), the sound velocity changes markedly with a decrease in the water content in the hydrogel. In these cases, it is hard to determine breaking points from *Figure 5*. As for the remaining three samples with 1/1, 2/1 and 3/1 NAPA/PAA ratios, breaking points are clearly observed, and the breaking points occur at higher water contents for higher NAPA contents. In other words, the amount of bound water in the hydrogel depends on the NAPA/PAA composition.

DISCUSSION

Sound velocity and compressibility give information about the states of the water and the polymers constituting the gel network. The change in sound velocity is caused mainly by the change in the compressibility of the water in the gel, since the compressibility of the polymer itself is considered to be unchanged. The adiabatic compressibility is defined as

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_s \tag{3}$$

where s is entropy. If the volume of the hydrogel is assumed to be the sum of the volumes for the network polymer and water, the compressibility of the hydrogel can be represented by

$$\beta = \phi_p \beta_p + \phi_w \beta_w \tag{4}$$

where ϕ is the volume fraction and the subscripts p and w indicate the network polymer and water, respectively. The adiabatic compressibility of the dry gel was estimated to be 0.78×10^{-10} Pa^{-1} from the sound velocity and density data. For a water content of less than 40 wt%, the adiabatic compressibility of the hydrogel results from the compressibility of the crosslinked polyacrylate polymer and the bound water. If the additivity of the compressibilities in the hydrogel holds for the volume fractions, as expressed in equation (4), the adiabatic compressibility of the bound water can be estimated from the adiabatic compressibility data in *Figure 3*. The adiabatic compressibility of the bound water is estimated to be 1.6×10^{-10} Pa^{-1}. The adiabatic compressibility of bulk water is 4.41×10^{-10} Pa^{-1} at 30°C and that of ice is 1.18×10^{-10} Pa^{-1} at 0°C[9]. The adiabatic compressibility of the bound water lies between the compressibilities of ice and bulk water. In other words, water bound in the gel is different from water in ice and is slightly softer than ice. Several d.s.c. investigations of hydrogels using a wide range of water contents indicate that the bound water consists of freezable and non-freezable water[1-7]. However, these two states of bound water cannot be distinguished by the measurement of sound velocity or adiabatic compressibility. A method using ultrasound can only determine the total amount of bound water.

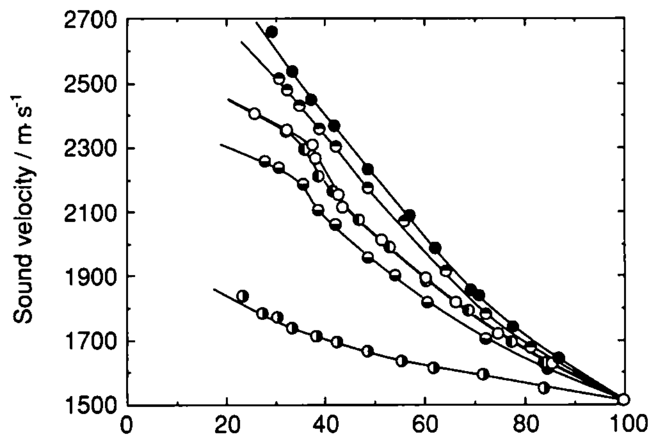

Figure 5 Plots of sound velocity *versus* water content at 30°C for different NAPA/PAA ratios: (◑) 0/1; (◒) 1/1; (◐) 2/1; (○) 3/1; (◓) 9/1; (●) 19/1

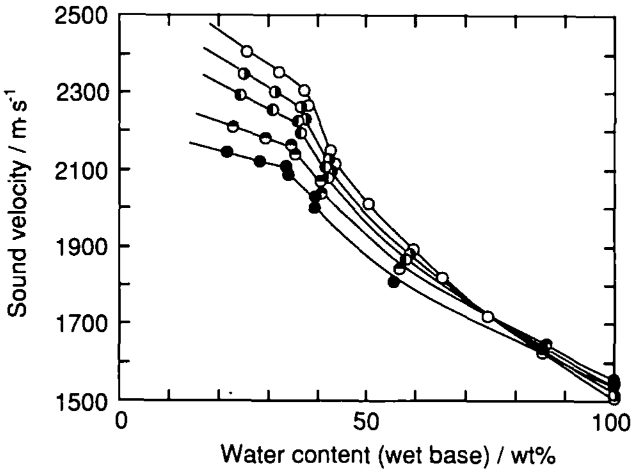

Figure 6 Plots of sound velocity *versus* water content in 3/1 NAPA/PAA for different temperatures: (○) 30°C; (◑) 40°C; (◐) 50°C; (◒) 70°C; (●) 90°C. The sound velocities were estimated from *Figure 4*

In *Figure 6*, the sound velocities at different temperatures are plotted against water content. The difference between the sound velocities in water and in the dry gel becomes smaller with increasing temperature. A breaking point in the sound velocity is observed at every temperature and it shifts to lower water content with increasing temperature. The presence of breaking points in *Figure 6* indicates that the two states of water exist in the hydrogel even at very high temperatures. The shift in the breaking point indicates that the amount of bound water decreases with increasing temperature.

It is difficult to determine the hydration numbers of solutes or ions in an unambiguous way. The hydration number of the sodium ion is considered to be between 4 and 6 depending on the experimental method employed[31]. Høiland *et al.* estimated the hydration number of the sodium ion as 5.9 using partial molar volume data[32]. It is well known that some of the sodium ions in NAPA bind to polyacrylate ions. The hydration number of the sodium ion bound to the polyacrylate ion through ion binding decreases[33] by 3–4. If only the sodium ion contributes to the hydration of sodium polyacrylate, the amount of hydration of the polyacrylate should be 0.36–0.56 g per gram of NAPA. The hydration of a hydrogel with a 3/1 NAPA/PAA ratio is 0.27–0.42 g per gram of gel, which is smaller than the amount of bound water estimated from the sound velocity data. The amount of bound water in sodium polyacrylate gel accordingly depends on factors such as the hydration of the sodium ion, the gel structure and the interaction between the polyion and water. The different compositions of PAA and NAPA lead to different degrees of swelling which are proportional to the inverse of the density of the crosslinking. The degree of swelling is roughly estimated by comparing the weight of a gel when swollen with its weight when dehydrated. The degree of swelling is 200 times for the composition ratio 0/1, 800 times for 3/1 and 600 times for 19/1. The degree of swelling reaches its maximum around a molar fraction of NAPA equal to 0.6, i.e. a 3/1 NAPA/PAA ratio. It is interesting to note that the breaking points in the sound velocities in *Figure 5* occur near the composition ratios producing the maximum degree of swelling.

Further investigation is required to elucidate the relationship between the sound velocity and the degree of swelling.

ACKNOWLEDGEMENTS

We would like to thank Toa Gohsei Chemicals for supplying the samples used to prepare the hydrogels.

REFERENCES

1 Lee, H. B., John, M. S. and Andrade, J. D. *J. Colloid Interface Sci.* 1975, **51**, 225
2 Sung, Y. K., Gergonis, D. E., John, M. S. and Andrade, J. D. *J. Appl. Polym. Sci.* 1981, **26**, 3719
3 Nakamura, K., Hatakeyama, T. and Hatakeyama, H. *Koubunshi Ronbunshu* 1982, **39**, 53
4 Nakamura, K., Hatakeyama, T. and Hatakeyama, H. *Polym. J.* 1983, **24**, 15
5 Nakamura, K., Hatakeyama, T. and Hatakeyama, H. *Polymer* 1983, **24**, 871
6 Wilson, T. W. and Turner, D. T. *Macromolecules* 1988, **21**, 1186
7 Cha, W.-I., Hyon, S.-H. and Ikeda, Y. *Makromol. Chem.* 1993, **194**, 2433
8 Katayama, S. and Fujiwara, S. *J. Am. Chem. Soc.* 1979, **101**, 4486
9 Katayama, S. and Fujiwara, S. *J. Phys. Chem.* 1980, **84**, 2320
10 Maquet, J., Theveneau, H., Djabourov, M., Leblond, J. and Papon, P. *Polymer* 1986, **27**, 1103
11 Tanaka, H., Fukumori, K. and Nishi, T. *J. Chem. Phys.* 1988, **89**, 3365
12 Quinn, F. X., Kampff, E., Smyth, G. and McBrierty, V. J. *Macromolecules* 1988, **21**, 3191
13 Smyth, G., Quinn, F. X. and McBrierty, V. J. *Macromolecules* 1988, **21**, 3198
14 Nosaka, A. Y., Ishikiriyama, K., Todoki, M. and Tanzawa, H. *J. Appl. Polym. Sci.* 1990, **39**, 2443
15 Nosaka, A. Y. and Tanzawa, H. *J. Appl. Polym. Sci.* 1991, **43**, 1165
16 Vanderwal, J., Sidebottom, D., Walton, D. and Jottari, G. P. *J. Polym. Sci., Polym. Phys. Edn* 1992, **30**, 1089
17 Odru, R., Rion, C., Vacher, J., Deterre, Ph., Peguin, P. and Vanoni, F. *Rev. Sci. Instrum.* 1978, **49**, 238
18 Nakajima, H., Tanaka, H., Shimazaki, O., Yamanaka, K., Kinoshita, T. and Wada, Y. *Jpn. J. Appl. Phys.* 1979, **18**, 1379
19 Matsuda, T. *Jpn. J. Appl. Phys.* 1981, **20**, 49
20 Koda, S., Yamashita, K., Matsumoto, K. and Nomura, H. *Jpn. J. Appl. Phys.* 1993, **32**, 2234
21 Saneyoshi, J., Kikuchi, Y. and Nomoto, O. 'Cho-onpa Binnran', Nikkan Kogyou Shinbunsya, Tokyo, 1966, p. 1353
22 Greenspan, M. and Tschiegg, C. E. *J. Res. Natl Bur. Stand.* 1957, **59**, 249
23 Sterling, C. and Tasuzawa, M. *Makromol. Chem.* 1968, **166**, 140
24 Kuntz Jr, I. D., Brassfild, T. S., Law, G. D. and Purcell, G. V. *Science* 1969, **163**, 1329
25 Woessner, D. E., Snowden Jr, B. S. and Chiu, Y. C. *J. Colloid Interface Sci.* 1970, **34**, 283
26 Dehl, R. E. *Science* 1970, **13**, 738
27 Mizuguchi, J., Takahashi, M. and Aizawa, M. *Nippon Kagaku Zasshi* 1970, **91**, 723
28 Aizawa, M. and Shuzuki, S. *Bull. Chem. Soc. Jpn.* 1971, **44**, 2967
29 Aizawa, M., Mizuguchi, J., Shuzuki, S., Hayashi, S., Suzuki, T., Mitomo, N. and Toyama, H. *Bull. Chem. Soc. Jpn.* 1972, **45**, 3031
30 Haldankar, G. and Spencer, H. G. *J. Appl. Polym. Sci.* 1989, **37**, 3137
31 Franks, F. (Ed.) 'Water', Vol. 3, Plenum Press, New York, 1973
32 Høiland, H., Ringseth, J. A. and Brun, T. S. *J. Solution Chem.* 1979, **8**, 779
33 Koda, S., Nomura, H. and Nagasawa, M. *Biophys. Chem.* 1985, **23**, 147